

# Studies to Improve the Wear Durability of Polytetrafluoroethylene (Teflon) Coatings on Elastomeric Vulcanizates

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## ABSTRACT

Methods for improving the wear durability of polytetrafluoroethylene (TFE) coatings on vulcanized elastomeric substrates have been investigated. A high-temperature flame-sintering technique has been developed which substantially improves the abrasion resistance of the TFE coatings, even in contact with rough surfaces such as 12-oz duck canvas. The flame-sintered TFE coatings exhibited a high order of durability in contact with smooth steel and anodized aluminum surfaces. Nonanodized aluminum surfaces were severely abraded by the TFE coatings. The flame-sintering treatment did not appreciably degrade the physical properties of most of the elastomers studied, nor did it adversely affect the frictional properties of the TFE coatings. Stabilizers utilized in gum neoprene and acrylonitrile elastomers tended to interfere in the adhesion of the TFE coating, but cleaning the surface of the vulcanizate with an aromatic solvent prior to application of the coating improved the adhesion.

A thin evaporated reflective aluminum film on the elastomer substrate provided an effective interfacial heat barrier for sintering TFE coatings with infrared heat. Vulcanizates coated only with TFE were burned and charred using this heat source. More work is needed, however, to improve the abrasive resistance of this combination of coatings.

The addition of colloidal boehmite alumina to the aqueous TFE dispersion significantly improved the abrasion resistance of sintered TFE coatings on elastomeric vulcanizates. Self-healing of cracks characterizes these coatings, which accounts in part for the improved wear resistance. Where cracks were present in coatings not containing this additive, peeling of the coating from the substrate was initiated at the edges of the cracks by abrasive wear.

The TFE and sintered TFE coatings were comparable in frictional properties but greatly superior in abrasion resistance to a proprietary TFE-filled-resin dry lubricant developed especially for application to rubber items.

## PROBLEM STATUS

This is an interim report on one phase of the problem; work on the problem is continuing.

## AUTHORIZATION

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# STUDIES TO IMPROVE THE WEAR DURABILITY OF POLYTETRAFLUOROETHYLENE (TEFLON) COATINGS ON ELASTOMERIC VULCANIZATES

## INTRODUCTION

Polytetrafluoroethylene (TFE), a relatively soft, waxy solid, has found widespread use as a dry lubricating material on metal surfaces (1). An earlier report (2) from this Laboratory described TFE coatings on elastomeric vulcanizates which were applied by spray techniques using commercial aqueous TFE dispersions. The thin TFE coatings provided surfaces having substantially lower coefficients of friction than the characteristic high values obtained with elastomeric vulcanizates. However, the TFE coatings have a limited wear resistance when subjected to abrasive action as might be encountered, for example, when they are used as dry lubricants in dynamic systems. It is believed this limited wear resistance is attributable both to the lack of adhesion of the TFE coating to the substrate and to the lack of cohesion between the particles of TFE which make up the coating.

These deficiencies are readily overcome with similar coatings on metal by heating the item in an oven at 680° to 750°F (360° to 400°C). This treatment improves the wear resistance by increasing adhesion to the substrate and by coalescing or sintering the TFE particles into a more continuous film, thereby increasing the cohesive strength of the coating.

The sintering of such TFE coatings is a time-temperature process, since the TFE is a poor thermal conductor and requires a finite time for the TFE particles to reach the sintering temperature. Depending on the type of heating, thickness of coating, and the nature of the substrate, the required time will vary from a few seconds to 20 to 30 minutes.

Because of the relatively low thermal resistance of elastomeric materials and, as a consequence, their inability to sustain the time-temperature conditions required for oven fusing of the TFE particles, other techniques were investigated at this Laboratory for sintering TFE coatings on elastomeric vulcanizates. A method for sintering TFE coatings on elastomeric substrates which involves the use of a carefully controlled high-temperature flame has been developed. This significantly increases the abrasion resistance of the TFE coating without appreciably degrading the physical properties of the elastomeric substrate or affecting the surface frictional properties of the coating. The feasibility of interposing a thin, reflective, aluminum film between the elastomer substrate and the TFE coating as a protective thermal barrier when utilizing radiant heat for sintering the coating has also been studied.

Finally, a substantial improvement in wear resistance of the TFE coating was achieved by the addition of colloidal boehmite alumina to the aqueous TFE emulsion before spraying the coatings. This effect was first noted by FitzSimmons and Zisman (3) when boehmite alumina was added to TFE coatings on metal bearings.

## MATERIALS AND TFE COATING PROCEDURE

The elastomers evaluated as substrates for the TFE coatings are listed in Table 1. The compound recipes are given in Table 2. The recipes were chosen so as to exclude

Table 1  
Elastomers Used for Polytetrafluoroethylene Coating Experiments

Elastomer	Description
NR	Natural rubber
SBR	Styrene-butadiene copolymer
Neoprene GNA*	Polychloroprene
NBR	Acrylonitrile-butadiene copolymer (medium acrylonitrile)
Viton B*	Vinylidene fluoride-hexafluoropropylene copolymer
Silicones	1. Polymethylvinylsiloxane 2. Fluoroalkylsiloxane with attached vinyl groups

\*E.I. du Pont de Nemours & Co., Inc.

materials which might bloom to the surface and interfere with the adhesion of the TFE coating, with the exception of the SBR elastomer which was compounded from a standard recipe.

The TFE dispersion used in the coating experiments was du Pont 851-204 TFE-Fluorocarbon Resin One-Coat Enamel.\* It was applied to acetone- or benzene-cleaned  $6 \times 6 \times 0.075$  in. molded tensile slabs with a DeVilbiss P-EGA-502 hand spray gun fitted with a No. 390 air cap. The coated specimens were air dried 24 hours, then heated in an oven for 2 hours at  $50^\circ\text{C}$ . Control of the coating thickness was important, because too thick a coating developed "mud-cracking" on drying. A dull, green-colored surface was a "rule-of-the-thumb" indication of the optimum coating thickness of 0.0003 to 0.0004 in. It was essential in applying the coating that the elastomer surface be completely covered, since any exposed area would be rapidly decomposed at the high temperatures required for the subsequent sintering process.

## TEST PROCEDURES

Standard ASTM procedures using an Instron Tensile Tester Model TTC were followed for measuring the tensile strength, tensile modulus, and elongation of the experimental specimens. Hardness was determined with a Shore A durometer gage.

A modified Taber abraser, shown in Fig. 1, was used to compare the wear properties of sintered and nonsintered TFE-coated specimens. The abrasive wheels of the Taber machine were replaced with aluminum wheels covered with strips of 12-oz duck canvas, so that the canvas could be renewed easily after each 500 cycles to present a fresh abrasive surface. A load of 1000 g was applied to each wheel, and the table rotation speed was 70 rpm..

The coefficients of friction of the TFE-coated specimens were obtained with a modified Bowden-Leben "stick-slip" apparatus.† Essentially, this machine measures the frictional force generated between a steel sphere and a reciprocating flat specimen surface.

## FLAME SINTERING OF TFE COATINGS ON ELASTOMERIC VULCANIZATES

The procedure for flame sintering the TFE coatings on elastomeric substrates is quite simple and consists of carefully passing a high-temperature flame in a reciprocating

\*E.I. du Pont de Nemours & Co., Inc.

†The apparatus is described in detail in NRL Report 5911.

Table 2  
Elastomer Compound Formulations Used as Substrates for TFE Coatings

Components	NR Pale Crepe	SBR Philprene 1500 F*	CR Neoprene GNA†	NBR Hycar 1011‡	Viton B†	Silicone		
						LS422§	LS63U§	433 Base§
	Parts per hundred rubber							
Stearic acid	4	1	1	1				
Bondogen¶		2						
Para Flux**		3						
Agerite Stalite¶		1						
Ethyl selenac¶		0.3						
Altax¶		0.5						
Captax¶	0.5							
Sulfur	3.5	2						
MgO			4		15			
ZnO	6	3	5	5				
MT black					20			
P-33 black¶			120					
EPC black (NBS)	40	70						
Pelletex††				5				
Hi-Sil 233‡‡				50				
Cab-O-Sil††						20	10	20
Dixie clay¶	150	80						
R. O. iron oxide§§						2	2	
Di-cup 40C¶¶				4.4				
LD-214†					3			
Silastic catalyst S-2084§						4	4	4
Cure:	45 min @ 300°F	20 min @ 307°F	45 min @ 310°F	45 min @ 310°F	30 min @ 300°F	15 min @ 340°F	15 min @ 340°F	15 min @ 340°F
Post-cure:					24 hr @ 400°F	16 hr @ 392°F	16 hr @ 392°F	16 hr @ 392°F

\*Philips Chemical Company.

†E.I. du Pont de Nemours & Co., Inc.

‡B.F. Goodrich Chemical Co.

§Dow Corning Corp.

¶R.T. Vanderbilt Co., Inc.

\*\*C.P. Hall Co.

††Godfrey L. Cabot, Inc.

‡‡Columbia-Southern Chemical Corp.

§§C.K. Williams & Co.

¶¶Hercules Powder Co., Inc.

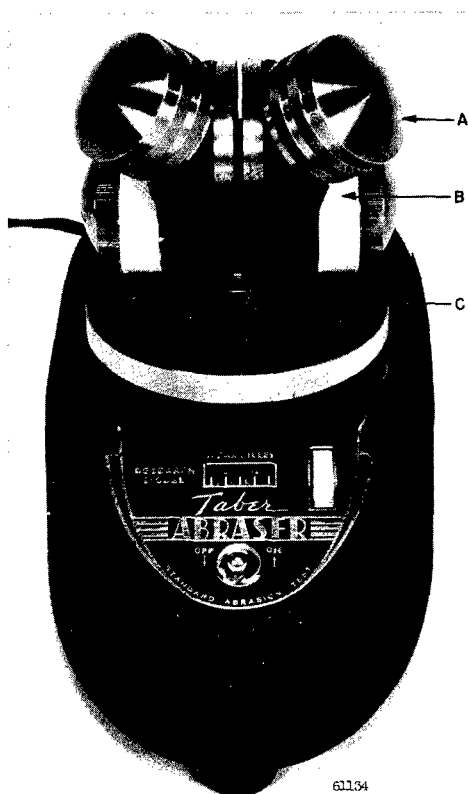


Fig. 1 - The modified Taber abra-  
ser used for testing abrasion  
resistance of TFE coatings on  
elastomer vulcanizates: (A) load  
weights, (B) canvas-covered abra-  
sion wheels, (C) specimen

motion over the coated surface. A National Welding Equipment Company Type 3A blowpipe torch fitted with an N-2 nozzle was used, in most cases with a natural gas-air mixture. The torch was adjusted to give a flame approximately 1-1/2 in. long with the flame cone extending 1 in. from the end of the nozzle. The flame temperature 1/8 in. from the end of the cone was 2660°F (1460°C) as measured with a platinum/platinum-rhodium thermocouple. Holding the torch so that the cone of the flame was roughly 1/8 in. from the specimen surface, the flame was moved back and forth across the specimen until on the second or third pass a change in the color of the specimen surface occurred just behind the flame. This change in color or shading signified the TFE coating was sintered and the flame was then moved to an adjacent nonsintered area and the process repeated until the entire surface had been treated. Other criteria which indicated proper fusion of the coating were the change from a hydrophilic to a hydrophobic surface and the resistance of the coating to removal by pressure-sensitive tape. The latter test consists of firmly pressing the tape on the coating and rapidly pulling it off. When properly sintered, the coating will not be removed from the substrate by the tape.

The sintering process obviously is more an art than a science, but skill in manipulating the flame to obtain reproducible results is easily acquired. Gas-oxygen flame mixtures may be used, but the hotter flame requires a faster rate of flame travel over the specimen and more careful control of flame distance from the surface. This is necessary to avoid excessive

expansion of the elastomeric substrate, which tends to promote cracks in the coating. The sintering operation should be carried out in a good hood, since the fumes from the pyrolytic degradation of TFE are quite toxic.

The flame-sintering process was successfully applied to four of the six types of elastomers evaluated. The TFE coating on natural rubber cracked excessively during the sintering process which exposed the substrate to the flame, resulting in reversion of the rubber. Thermal expansion of the silicone substrate also produced excessive cracking of the TFE coating resulting in poor wear performance. It is possible that compounding studies to reduce the thermal expansion of these two elastomers would render them suitable as substrates for sintered TFE coatings. However, studies of this nature were not undertaken in this program.

#### EFFECT OF THE FLAME TREATMENT ON THE PHYSICAL PROPERTIES OF THE TFE-COATED ELASTOMERS

The TFE dispersions used for spraying the coatings contain surfactants and possibly other organic materials which are volatilized by the flame treatment. The average weight loss produced by the flame treatment of TFE-coated elastomers was determined indirectly

by flame sintering TFE coatings on metal substrates. The weight loss for the coatings on metal substrates was 13.3%. A similar weight loss is assumed for the data given in Table 3 for sintered coatings on elastomeric substrates. These data indicate the substrate weight loss to be less than 0.1% for four types of elastomers.

The change in the physical properties of the four types of successfully treated coated elastomers are summarized in Table 4. The most seriously affected were SBR and Neoprene GNA, but the maximum losses sustained in tensile strength and elongation were less than 20%. The change in hardness of all the specimens was negligible.

Table 3  
Elastomer Substrate Average Weight Loss Resulting  
from the TFE Coating Flame-Sintering Treatment

Elastomer	Average Weight Loss (%)
NBR (Hycar 1011)	0.06
Viton B	0.03
Neoprene GNA	0.05
SBR (Philprene 1500 F)	0.08

Table 4  
Percent Change in Physical Properties of the Elastomer Substrate  
Resulting from the TFE Coating Flame-Sintering Treatment

Elastomer	Percent Change in Physical Properties		
	Durometer Hardness	Tensile Strength	Elongation
NBR (Hycar 1011) (Shore A hardness = 85)	No change*	-5.2	No change
SBR (Philprene 1500 F) (Shore A hardness = 85)	No change*	+18.0	No change
Neoprene GNA (Shore A hardness = 85)	No change*	+9.5	-13.2
Viton B (Shore A hardness = 65)	No change*	+4.6	+7.4
Viton B (Shore A hardness = 75)	No change*	-3.7	-4.8

\*Within  $\pm 5$  Shore A units.

#### EFFECT OF SINTERING PROCESS ON THE WEAR BEHAVIOR OF TFE-COATED ELASTOMERS

The amount of wear sustained by the TFE-coated elastomers under the abrasive action of the canvas-coated wheels of the Taber abraser was difficult to measure quantitatively. Weighing the specimens before abrasive runs was too time consuming, because conditioning at 72°F and 50% R.H. required 6 days to reach moisture equilibrium and constant weight. Therefore, the relative wear between nonsintered and sintered specimens was empirically determined by visual observations and study of photomicrographs. Rough comparisons were made of the number of cycles a specimen underwent before showing excessive wear. In most instances, the maximum test was 10,000 cycles.

A number of factors in addition to the sintering were observed to influence the wear resistance of the TFE-coated elastomers. These were the nature of the elastomer substrate (i.e. hardness, presence of stabilizers), the nature of the coating (continuity), and the character of the surface in contact with the coating (rough or smooth).



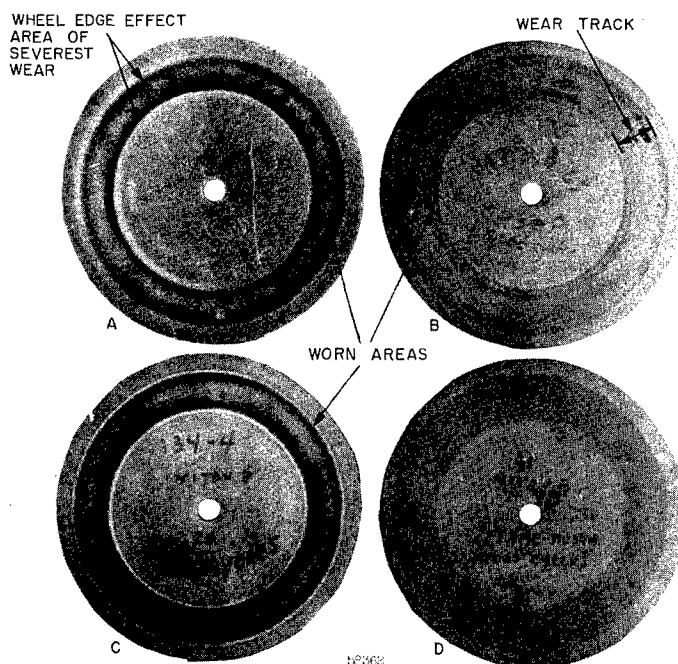


Fig. 2 - Comparison of the effects of wear on nonsintered and sintered TFE-coated Viton B specimens having two different substrate hardnesses after 10,000 cycles on the Taber abraser: (A) nonsintered, Shore A hardness = 65; (B) flame sintered, Shore A hardness = 65; (C) nonsintered, Shore A hardness = 75; (D) flame sintered, Shore A hardness = 75

The effects of sintering and of the hardness of the elastomeric substrate are illustrated in Fig. 2. This shows the relative wear after 10,000 cycles on the Taber abraser of nonsintered and sintered TFE-coated Viton B specimens and compares two substrate hardnesses. Specimens A and C were not sintered, and B and D were flame sintered. Maximum wear always occurred at the inner and outer edges of the wear track because of an edge effect, and the least wear took place in the center of the track. The dark areas on the photograph of the wear track indicate excessive wear. In most cases, even though the coating appears in some areas to be worn completely off the substrate, a thin film remains, as shown by friction measurements. Both of the sintered specimens (B,D) show considerably less wear than their nonsintered counterparts (A,C). Greater wear is evident on the softer specimens, but the harder specimen (D) showed essentially no wear after 10,000 cycles. The abrasion resistance of the flame-sintered TFE coating on Viton B is higher than on any other elastomeric substrate evaluated.

The relative improvements in wear resistance realized by the flame-sintering process are further illustrated in Fig. 3, which is a photograph of nonsintered and sintered TFE coatings on SBR substrates having a Shore A hardness of 85. This elastomer is an inexpensive, general-purpose rubber used extensively in numerous applications; it was compounded from a standard recipe. After 10,000 wear cycles on the Taber abraser, the sintered specimen exhibited substantially less wear than its nonsintered counterpart after 5000 cycles. Sintered TFE coatings had greater wear resistance on harder substrates than on softer ones, but both were superior to nonsintered specimens, regardless of hardness.

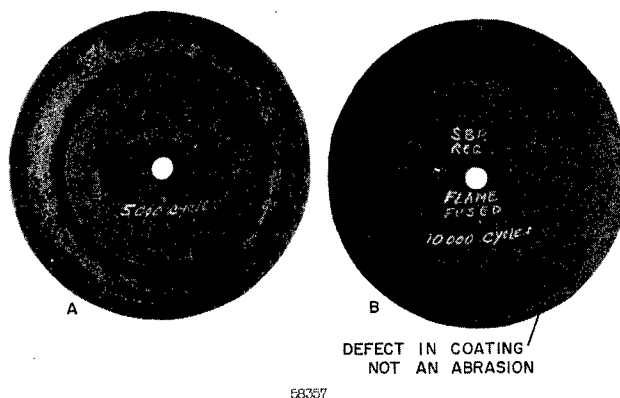


Fig. 3 - Abrasion resistance of TFE coatings on acrylonitrile (SBR) vulcanizates, Shore A hardness of substrate = 85: (A) nonsintered specimen after 5000 cycles on the Taber abraser, (B) flame-sintered specimen after 10,000 cycles on the Taber abraser

Butadiene-acrylonitrile elastomers (Hycar 1011) coated with TFE are shown in Fig. 4 after wear tests on the Taber abraser. The appearance of the nonsintered specimen after only 3500 cycles contrasts sharply with the flame-sintered specimen after 8000 cycles. The abrasive resistance of this coated elastomer was further improved by postcuring the stock for 24 hours at 300°F before coating. This treatment apparently volatilizes the amine stabilizer present in the original gum stock. Less wear was observed on the postcured specimens, which indicated that the amine stabilizer was interfering with adhesion of the coating to the substrate. The mode of wear on the nonsintered and nonpostcured specimens was characterized by a peeling away of the coating from the substrate, while the coating on the postcured specimen appeared merely to be wearing thin from the abrasive action.

Usually, the vulcanized substrate surface was cleaned by swabbing it with acetone. A substantial improvement in the wear resistance of TFE-coated neoprene GNA results, however, if the surface is cleaned with benzene, which is apparently a more efficient solvent for removal of the thiuram stabilizer always present in this elastomer. An even greater improvement may be realized by a xylene-extraction treatment of the vulcanizate to remove some of the stabilizer. The relative effects of the three methods of preparing the neoprene substrate surface on the wear resistance of the TFE coating are shown in Fig. 5. Fifteen hundred cycles on the Taber abraser produced excessive wear of the coating on the acetone-cleaned specimen, while the benzene-cleaned specimen sustained 5000 cycles before a comparable amount of wear was observed. The xylene-extraction treatment increased the wear resistance another 3000 cycles, but it caused the elastomer elongation to be reduced by one third.

The abrasion resistance of sintered TFE coatings on a natural rubber substrate was poor, and severe wear occurred after 1000 cycles. Microscopic examination revealed that mud-cracking of the TFE coating had resulted from the sintering process. A hotter flame and faster rate of flame travel improved the wear resistance but did not eliminate the mud-cracking. The wear on this type of surface was characterized by the TFE being removed by a "balling-up" of the coating as the wheel moved over the surface. This balling phenomenon was initiated at the edges of the cracks in the coating, indicating poor



Fig. 4 - Effect of postcuring (300°F for 24 hr) the substrate prior to application of the coating on the abrasion resistance of TFE-coated NBR vulcanizates, Shore A hardness = 85: (A) non-sintered control after 3500 cycles on the Taber abraser, (B) flame-sintered control after 8000 cycles on the Taber abraser, (C) postcured, nonsintered specimen after 2000 cycles on the Taber abraser, (D) postcured, flame-sintered specimen after 10,000 cycles on the Taber abraser

adhesion between the coating and the substrate. A substantial degradation of the physical properties of the natural rubber substrate also resulted from the flame treatment.

The flame sintering of TFE coatings on silicone substrates was unsuccessful because of excessive cracking of the coating on application of the flame. It is believed that the notoriously high thermal coefficient of expansion of this elastomer was responsible for such behavior.

The effect on wear resistance of the type of abrading surface in contact with the TFE coating is illustrated in Fig. 6 which shows a sintered TFE-coated 85 Shore A hardness neoprene GNA specimen after 50,000 cycles on the Taber abraser in contact with smooth steel rollers. Little, if any, of the TFE coating had been removed, and the only manifestation of coating wear was a highly polished surface. Similar wear behavior was observed using anodized aluminum wheels. These are probably the types of contact surfaces which would be used in many applications where TFE-coated elastomers might be used. In these cases, some of the TFE transfers to the smooth metal surface, and a condition of TFE rubbing on TFE exists. On the other hand, severe abrasion of the metal surface occurred when wear tests were made with smooth nonanodized aluminum wheels in contact with the TFE-coated elastomer. This phenomenon has been observed elsewhere, with TFE bearings in contact with aluminum alloy shafts (4).

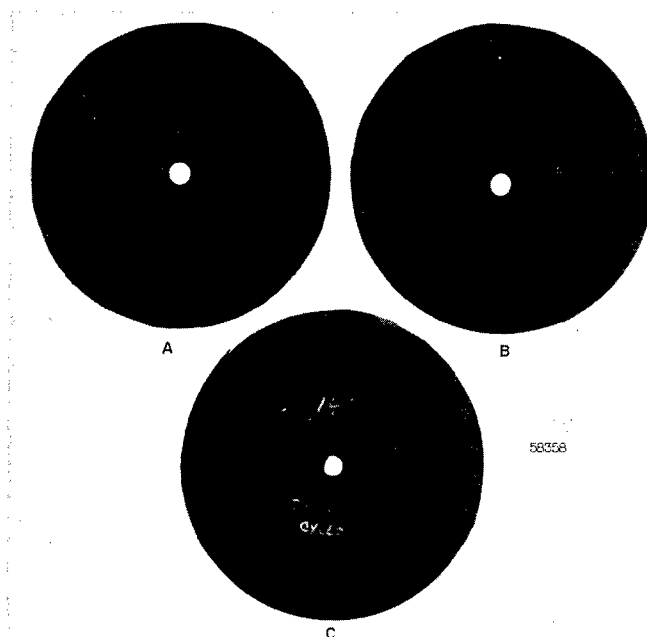
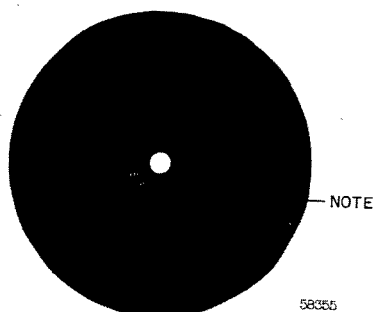


Fig. 5 - Effect of various methods of cleaning the surface of the substrate prior to coating on the abrasion resistance of flame-sintered TFE-coated neoprene GNA: (A) acetone-cleaned specimen after 1500 cycles on the Taber abraser, (B) benzene-cleaned specimen after 5000 cycles on the Taber abraser, (C) xylene-extracted specimen after 8000 cycles on the Taber abraser

Fig. 6 - A flame-sintered TFE-coated neoprene GNA vulcanizate (Shore A hardness = 85) after 50,000 cycles on the Taber abraser in contact with smooth steel wheels. Note: Not a wear spot; coating removed with knife edge after wear test



#### FRICITIONAL PROPERTIES OF SINTERED TFE-COATED ELASTOMERS

Essentially identical values for the dynamic coefficients of friction were obtained on both nonsintered and sintered TFE-coated elastomeric vulcanizates having the same substrate hardness, as measured with the NRL-modified "stick-slip" machine. Typical values are shown graphically in Fig. 7 for the TFE-coated Viton B elastomer of 75 Shore A hardness. Curves representing the values for the dynamic coefficient of friction obtained on uncoated vulcanized Viton B having the same hardness and on a flame-fused TFE-coated

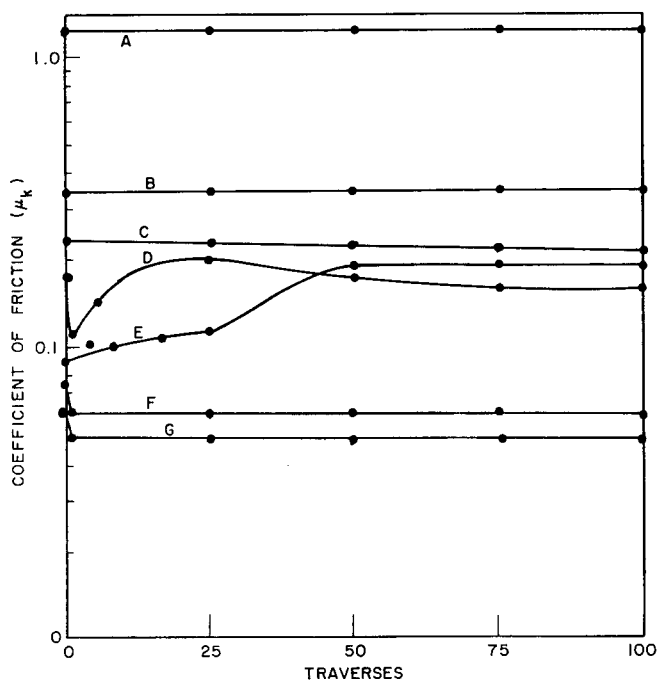


Fig. 7 - Comparison of the dynamic coefficient of friction of TFE-coated Viton B vulcanizates with that of an uncoated vulcanizate and of sintered TFE-coated steel before and after wear on the Taber abraser: (A) uncoated Viton B, (B) nonsintered TFE-coated Viton B after 10,000 cycles, (C) sintered TFE-coated Viton B after 10,000 cycles, (D) nonsintered TFE-coated Viton B, no wear, (E) sintered TFE-coated Viton B, no wear, (F) sintered TFE-coated steel after 10,000 cycles, (G) sintered TFE-coated steel, no wear

steel specimen are included for purposes of comparison. The substantially lower coefficient of friction exhibited by the coated metal specimen is attributable to the effect of the greater hardness of the substrate which bears the bulk of the load with little deformation, resulting in a low value for the real area of contact (1). Usually, the initial frictional values were lower on the sintered surfaces; but after 50 traverses of the metal slider, they increased to approximately the same as those for the nonsintered surface.

In every case, an increase in the values for the coefficients of friction was observed after wearing in on the Taber abraser; i.e., frictional values on the wear track were higher than on surfaces which had not been subjected to wear. In this case, the asperities of the TFE coating were flattened by the wheels, and the real area of contact of the stick-slip machine slider on the worn surfaces was greater than on the nonabraded surface. The photomicrographs in Fig. 8 of the TFE surfaces before and after wear on the Taber abraser clearly show this flattening of the surface asperities. The effect of increased surface area on the frictional behavior of TFE-coated surfaces is illustrated in Fig. 9 in which the coefficient of friction of TFE-coated neoprene GNA before and after 50,000 cycles on the Taber abraser using smooth steel wheels is plotted (Curves A and B). After these measurements, the specimen used for Curve B was abraded lightly with wet 600A silicon carbide paper, blotted, and dried in a desiccator; and the coefficient of friction was again determined in the same wear track. The values for the coefficient of friction were

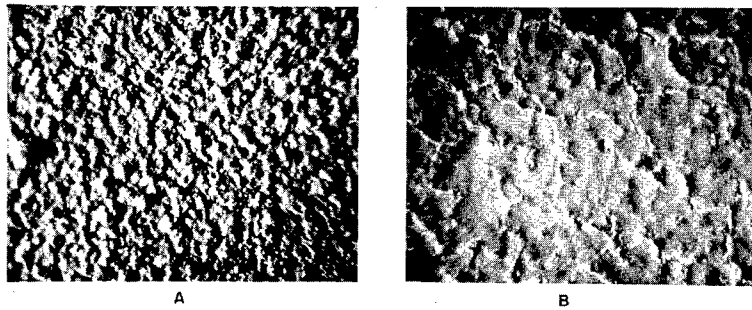


Fig. 8 - Photomicrographs of flame-sintered TFE-coated neoprene GNA vulcanizates showing surface contour changes resulting from wear on the Taber abraser using smooth steel wheels (original magnification = 60X): (A) TFE-coated surface before wear, (B) TFE-coated surface after 50,000 cycles

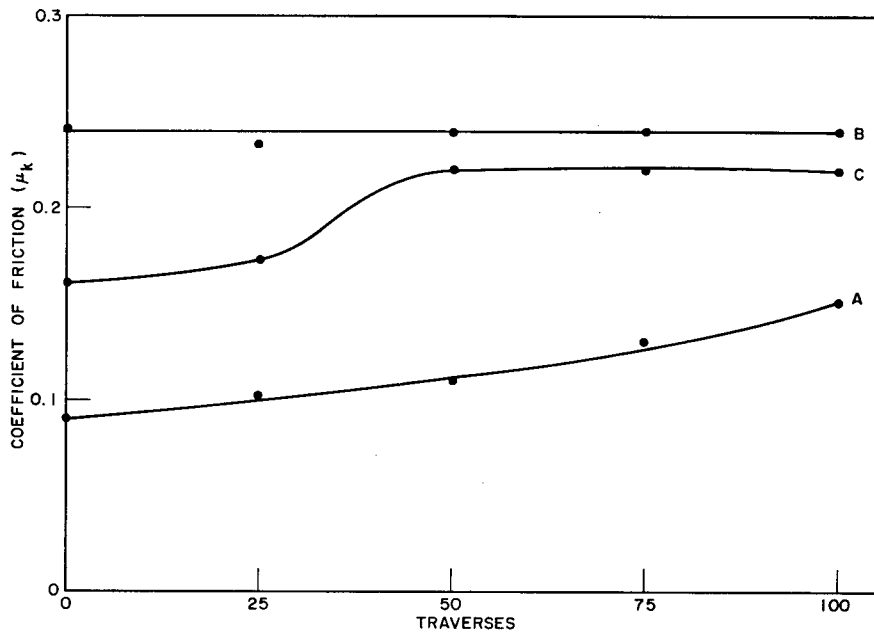


Fig. 9 - The effect of surface asperities on the dynamic coefficient of friction of sintered TFE-coated neoprene GNA vulcanizate: (A) dynamic coefficient of friction of specimen before wear on the Taber abraser, (B) dynamic coefficient of friction of specimen after 50,000 cycles on the Taber abraser using smooth steel wheels, (C) dynamic coefficient of friction of specimen B after friction wear track was roughened with moist 600A silicon carbide paper

decreased appreciably by the roughening of the TFE surface, but repeated traverses of the steel slider again flattened the asperities, which increased the real area of contact and the values for the coefficient of friction.

## SINTERING TFE COATINGS WITH INFRARED HEAT

The infrared technique of sintering the TFE coating on vulcanized elastomeric substrates was investigated less extensively and only on small specimens. The source of infrared heat was a chimney-type, bare-wire resistance heater, and the specimen was exposed through a slot in the top of the chimney.

Attempts to sinter elastomer specimens coated only with TFE by radiated heat always resulted in charring and burning of the elastomeric substrate. Even radiation temperatures up to 1000°F, obtained with a reflected quartz lamp, required so much time to reach the sintering temperature of the coating that charring of the elastomer substrate occurred. However, when a thin aluminum layer (600 to 1000Å thick) was formed on the elastomer substrate by vacuum evaporation and the TFE coating applied over the aluminum layer, sintering of the coating was accomplished easily with little or no degradation of the elastomer substrate. In this case, the bulk of the transmitted heat energy is reflected by the aluminum barrier back into the TFE coating; thus, the concentration of the heat energy results in more rapid heating of the TFE coating and keeps to a minimum the heat absorbed by the elastomer substrate. Figure 10 demonstrates the effectiveness of the aluminum layer (as a heat barrier) on a neoprene GNA vulcanizate. Three specimens are shown, one with no coating, one coated with TFE, and another coated with an aluminum film covered with TFE. The aluminum/TFE-coated specimen withstood 882°F for 2 minutes, while the other two specimens became warped and charred after only 1 minute at 775°F. Evidence that the TFE coating was sintered was obtained from the pressure-sensitive tape test. Figure 11 shows an aluminum/TFE specimen in which only a portion of the surface was sintered. The pressure-sensitive tape was pressed on both the non-sintered and sintered areas. The light-colored area represents removal of the TFE coating, exposing the aluminum undercoat. The dark area is the portion of the coated specimen which was exposed to the slot in the top of the bare-wire radiant heater. None of the sintered TFE coating was removed by the tape, indicating successful fusion of the coating. These experiments indicate that with proper design engineering and the use of a reflective aluminum heat barrier a practical system for sintering the TFE coating with radiant heat might be feasible.

The specimens sintered by the infrared technique were too small for wear tests on the Taber abraser. However, the abrasion resistance was determined on aluminum/TFE-coated vulcanizates sintered by the flame technique, and these were found to have much less abrasion resistance than those coated only with TFE. Primarily, failures occurred because of poor adhesion of the TFE to the aluminum film. In the cases of the silicone and neoprene elastomers, however, lack of adhesion of the aluminum film to the substrate resulted in low abrasion resistance. The best abrasion resistance, using aluminum/TFE-coated elastomers, was obtained with Viton, but even it showed severe wear after 3500 cycles. This did not compare with Viton specimens coated only with sintered TFE, which showed only minor wear after 10,000 cycles. Compounding studies and the use of other types of TFE dispersions would perhaps have improved the wear resistance of the aluminum/TFE coatings. However, these studies were not undertaken, since durable sintered-TFE coatings could be obtained without the aluminum film using the flame-sintering technique.

## EFFECT OF COLLOIDAL BOEHMITE ALUMINA ON THE WEAR BEHAVIOR OF TFE COATINGS

FitzSimmons and Zisman (3) have demonstrated that the addition of colloidal boehmite alumina to aqueous dispersions of TFE (du Pont Teflon (TFE) Green Primer 850-204) not only tended to stabilize the dispersion, but also reinforced the sintered films applied to metal substrates making the coatings more resistant to abrasion and cold-flow and more durable under conditions of localized frictional heating. The boehmite alumina used was a

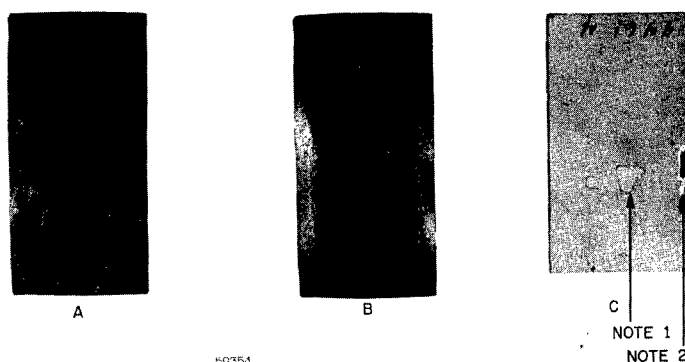


Fig. 10 - Photographs showing the effectiveness of a reflective interfacial aluminum film acting as a heat barrier for sintering TFE on elastomers with infrared heat: (A) neoprene GNA heated 1 minute at 775°F, (B) neoprene GNA coated with TFE and heated 1 minute at 775°F, (C) neoprene GNA with aluminum/TFE coatings heated 2 minutes at 882°F. Note 1: Water spot applied prior to heating. Note 2: Aluminum/TFE coatings removed with knife edge; not a burned spot.

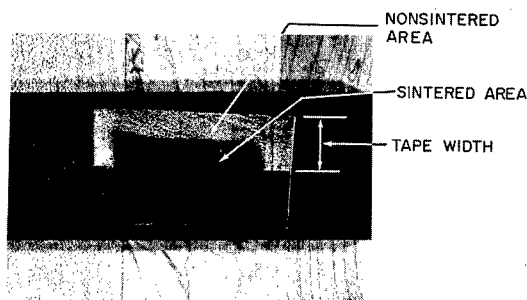


Fig. 11 - Results of pressure-sensitive tape test on an infrared-sintered aluminum/TFE-coated neoprene GNA vulcanizate

synthetic hydrated aluminum oxide ( $\text{AlOOH}$ ) produced by the du Pont Company and designated as Baymal.\* The particles are rod shaped with a length of about  $120 \text{ m}\mu$  and a diameter of approximately  $5 \text{ m}\mu$ . The specific area is  $293 \text{ m}^2/\text{g}$ . When dispersed in water, the particles normally are positively charged. The TFE particles in commercial aqueous dispersions are negatively charged, and the smaller positively charged needlelike Baymal particles are drawn onto the surface of the TFE particles by the attractive electrostatic charges until the charges are neutralized. This tends to establish strong cohesion between the Baymal-coated TFE particles, resulting in stronger TFE films.

\*Trademark, E.I. du Pont de Nemours & Co., Inc.



In the present work, the Baymal was added from a 10% dispersion to the du Pont 851-204 TFE-Fluorocarbon Resin One-Coat Enamel in the amount of 3 wt-% based on total solids content. The coatings were applied and sintered on a Viton B vulcanizate having a durometer hardness of 65. The softer substrate was chosen to better illustrate the effectiveness of the additive in promoting abrasion resistance of the coating. The specimen was subjected to 10,000 cycles on the Taber abraser using canvas-covered wheels. Figure 12 contrasts the abrasion of this specimen with one coated only with TFE. Substantial wear is evident on the latter specimen, while the one containing Baymal is relatively free of wear areas. The effect of the additive was less evident on an SBR vulcanizate having a durometer hardness of 85, since a sintered-TFE coating on a substrate of this hardness has inherently good wear durability.



Fig. 12 - Photographs showing the superior abrasion resistance of flame-sintered TFE coating containing 3% Baymal on a Viton B vulcanizate (Shore A hardness = 65): (A) flame-sintered specimen after 10,000 cycles on the Taber abraser, (B) flame-sintered specimen with TFE coating containing 3% Baymal after 10,000 cycles on the Taber abraser

All of the TFE coatings containing Baymal developed mud-cracks during the sintering process. This mud-cracking was considerably less pronounced in coatings on the Viton B vulcanizate than on SBR substrates. However, it is significant that peeling of the coating was not initiated at these cracks when they were subjected to abrasive wear, as was the case where cracks were present in coatings without Baymal. Rather, the Baymal appeared to promote self-healing of the cracks as the wear progressed. This phenomenon is illustrated in the photomicrographs in Fig. 13. Photomicrograph A shows the mud-cracks which result when too thick a coating is applied. Photomicrograph B illustrates the peeling of the coating which occurs from abrasive action. Photomicrographs C and D are of a specimen coating containing Baymal before and after abrasion on the Taber abraser.

#### EVALUATION OF A TFE-FILLED-RESIN DRY-FILM LUBRICANT AS A LOW-FRICTION COATING FOR ELASTOMERS

A proprietary commercial product developed as a dry-film lubricant for rubber items, and described as TFE in a water-dispersible resin, was evaluated on vulcanized SBR having a Shore A hardness of 80. The purpose of this experiment was to compare the frictional behavior and abrasion resistance of this material with the TFE and sintered

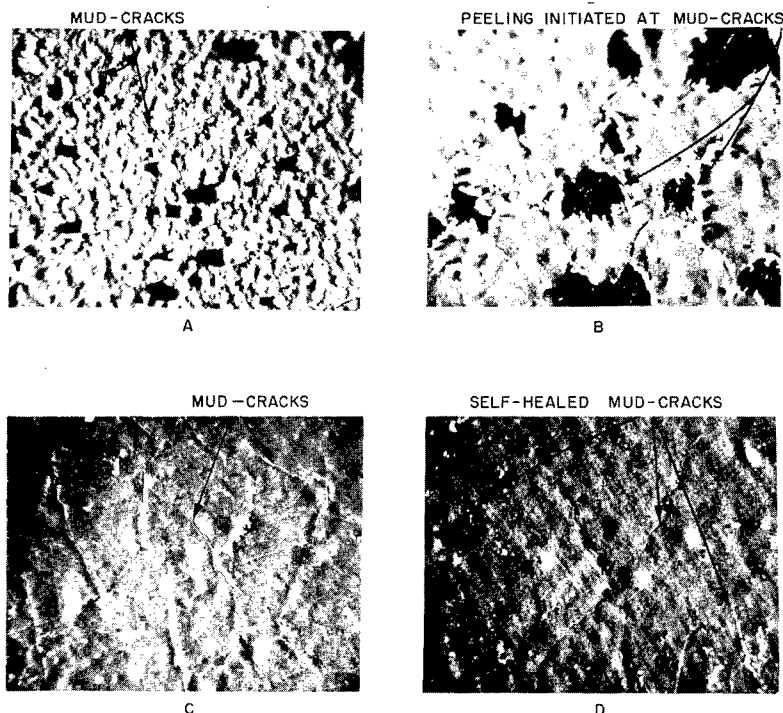


Fig. 13 - Photomicrographs illustrating the self-healing of cracks exhibited by sintered TFE coatings containing Baymal on SBR vulcanizates (Shore A hardness = 85): (A) imperfect TFE coating containing mud-cracks before abrasive action of the Taber abraser, (B) specimen A after wear on the Taber abraser, (C) mud-cracked specimens of TFE coating containing Baymal before abrasion on the Taber abraser, (D) specimen C after 10,000 cycles on the Taber abraser

TFE coatings described in this report. Curves depicting the frictional behavior of this proprietary coating are shown in Fig. 14. The values for the coefficient of friction compare favorably with those obtained with coatings applied from the aqueous du Pont 851-204 TFE dispersions. However, the abrasion resistance of the proprietary dry-film lubricant was greatly inferior to the nonsintered TFE coatings, lasting only 500 cycles on the Taber abraser using canvas-covered wheels. Flame sintering the proprietary film improved the durability of the coating about sixfold, enabling it to complete 3000 cycles before appreciable wear was evident. The nonsintered TFE coatings on an SBR substrate required 5000 cycles in the same test to induce comparable wear effects. The flame-sintered specimen completed 10,000 cycles with less damage to the coating than the flame-sintered proprietary film sustained with 3000 cycles. Flame sintering the resin-TFE coating increased the value of the initial coefficient of friction from 0.18 to 0.35

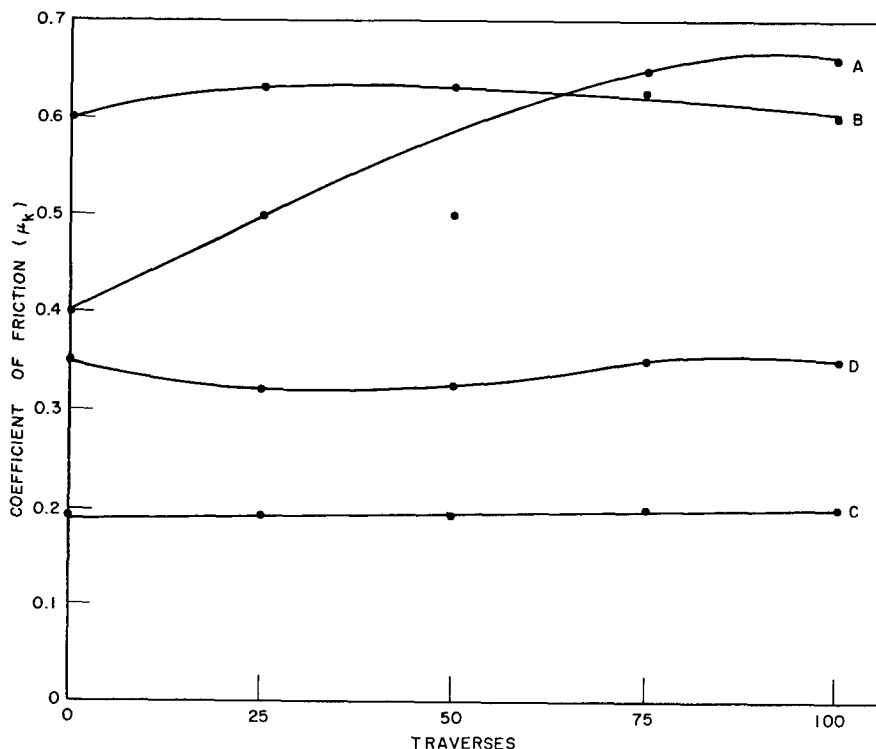


Fig. 14 - The dynamic coefficients of friction of nonsintered and sintered proprietary dry-lubricant film on SBR vulcanizates (Shore A hardness = 80) before and after wear on the Taber abraser: (A) dynamic coefficient of friction of nonsintered film after 500 cycles on the Taber abraser, (B) dynamic coefficient of friction of sintered film after 3000 cycles on the Taber abraser, (C) dynamic coefficient of friction of nonsintered film before wear test, (D) dynamic coefficient of friction of sintered film before wear test

physical properties of most of the elastomer substrates studied, nor does it adversely affect the frictional properties of the coating.

2. The flame-sintered TFE coatings on elastomer vulcanizates have a high order of durability in dynamic contact with smooth steel and anodized aluminum surfaces. Non-anodized aluminum surfaces are severely abraded in contact with the TFE-coated vulcanizates.

3. Stabilizers, such as used in gum neoprene and acrylonitrile elastomers, tend to reduce the adhesion of the TFE coating to the elastomer vulcanizates and consequently the wear resistance of the TFE coating. Adhesion of the coating is improved by cleaning the surface of the vulcanizate with an aromatic solvent (benzene) prior to applying the TFE coating. A xylene extraction of the stabilizer further improves the adhesion of the coating to the elastomer substrate, but the practicality of this treatment is questionable, since the physical properties of the elastomers are considerably degraded.

4. The coefficient of friction of the TFE-coated elastomers always increases to a limiting value as a result of wear. This is believed to be attributable to an increase in the real area of contact caused by a flattening of the surface asperities in the wear track.

5. A thin, reflective film of aluminum evaporated on an elastomeric vulcanizate provides an effective interfacial heat barrier so that the polytetrafluoroethylene coating can be sintered by radiated heat without degradation of the elastomer substrate. However, the abrasion resistance of the aluminum/TFE-coated vulcanizates studied was considerably lower than those coated only with TFE. Primarily, failure was due to poor adhesion of the TFE to the aluminum, except in the cases of neoprene and silicone elastomers where failure occurred between the aluminum film and the elastomer substrate.

6. The addition of colloidal boehmite alumina (Baymal) to the aqueous TFE dispersion significantly improves the wear resistance of sintered TFE coatings on elastomeric substrates. These coatings are characterized by self-healing of cracks in the coating, which accounts in part for the improved wear resistance. Cracks in TFE coatings which do not contain this additive tend to initiate peeling of the coating from the substrate when subjected to abrasive wear.

7. The TFE and sintered TFE coatings described in this report were comparable in frictional behavior but greatly superior in abrasion resistance to a proprietary TFE-filled-resin dry lubricant developed especially for application to rubber items.

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## DOCUMENT CONTROL DATA - R&amp;D

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		2b. GROUP	
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13. ABSTRACT Methods for improving the wear durability of polytetrafluoroethylene (TFE) coatings on vulcanized elastomeric substrates have been investigated. A high-temperature flame-sintering technique has been developed which substantially improves the abrasion resistance of the TFE coatings, even in contact with rough surfaces such as 12-oz duck canvas. The flame-sintered TFE coatings exhibited a high order of durability in contact with smooth steel and anodized aluminum surfaces. Nonanodized aluminum surfaces were severely abraded by the TFE coatings. The flame-sintering treatment did not appreciably degrade the physical properties of most of the elastomers studied, nor did it adversely affect the frictional properties of the TFE coatings. Stabilizers utilized in gum neoprene and acrylonitrile elastomers tended to interfere in the adhesion of the TFE coating, but cleaning the surface of the vulcanizate with an aromatic solvent prior to application of the coating improved the adhesion.  A thin evaporated reflective aluminum film on the elastomer substrate provided an effective interfacial heat barrier for sintering TFE coatings with infrared heat. Vulcanizates coated only with TFE were burned and charred using this heat source. More work is needed, however, to improve the abrasive resistance of this combination of coatings.  The addition of colloidal boehmite alumina to the aqueous TFE dispersion significantly improved the abrasion resistance of sintered TFE coatings on elastomeric vulcanizates. Self-healing of cracks characterizes these coatings, which accounts in part for the improved wear resistance. Where cracks were present in coatings not containing this additive, peeling of the coating from the substrate was initiated at the edges of the cracks by abrasive wear.  The TFE and sintered TFE coatings were comparable in frictional properties but greatly superior in abrasion resistance to a proprietary TFE-filled-resin dry lubricant developed especially for application to rubber items.			

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Polytetrafluoroethylene (Teflon) Abrasion resistance Elastomers Sintering Frictional properties Adhesion Cohesion Boehmite alumina						

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